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A Facile Conversion of α-Nitroepoxides into 1,2-Diones and α-Iodoketones

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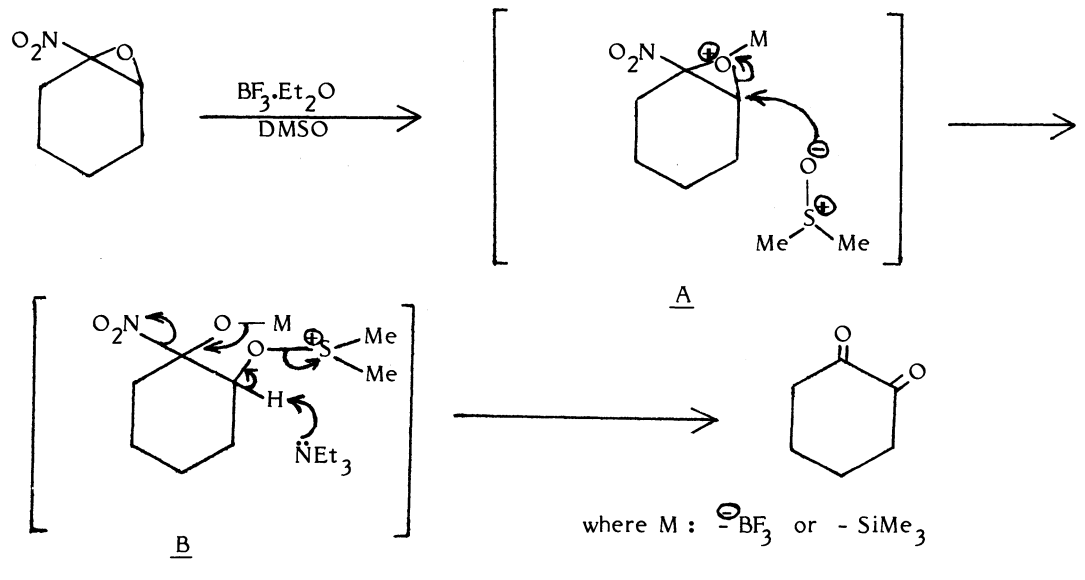
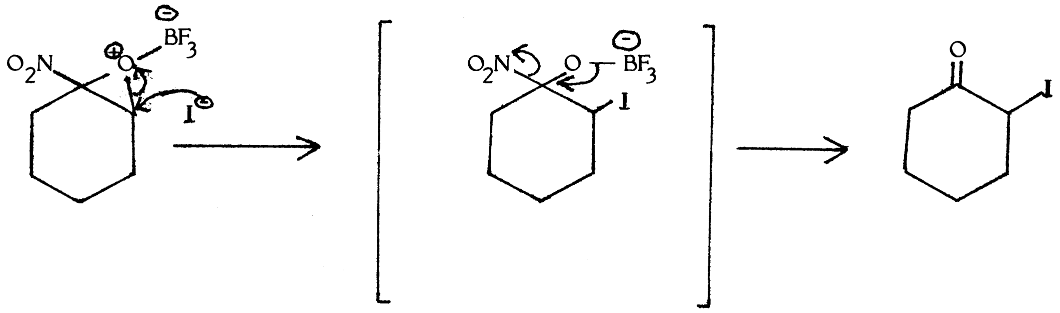
1,2-Diones and α-iodoketones have been prepared from α-nitroepoxides by treatment with DMSO/$BF_3.Et_2O$ followed by Et_3N and $BF_3.Et_2O$/NaI respectively.

1-2-Diones are important intermediates in organic synthesis. As a result a number of synthetic methods have been developed for their preparation.1) Recently we have reported2) a simple method for the preparation of 1,2-diones from α-nitroepoxides by their isomerisation with tetrakis (triphenylphosphine) palladium(O). In this paper we wish to report a yet simpler and milder approach for the conversion of α-nitroepoxides into 1,2-diones. This involves reactions of α-nitroepoxides with either $BF_3.Et_2O$ or $ClSiMe_3$ in the presence of DMSO followed by treatment of the intermediates formed with triethylamine. A tentative mechanism of this conversion is shown in Scheme 1. It is expected that a Kornblum type intermediate i.e. B is formed by the attack of DMSO on the intermediate A. Deprotonation of B, by triethylamine, followed by loss of dimethyl sulfide, and expulsion of the nitro group eventually affords the dione.



Scheme 1.

Results are summarised in Table 1. It is clear that these reactions are general and applicable to both acyclic as well as cyclic systems. Loss of a NO_2 group from an α-nitroepoxide as a result of the attack of a nucleophile has been reported earlier by other workers.[3—5] Additionally we have found that when α-nitroepoxides are treated with $BF_3.Et_2O$ in acetonitrile in the presence of NaI, α-iodoketones are formed in good yields (cf. see Table 1). This simply involves a nucleophilic attack of an iodide ion on the intermediate A (Scheme 2) with concommitant loss of the nitro group.



Scheme 2.

In view of the fact that both 1,2-diones[1)] as well as α-iodoketones[5)] are important intermediates in organic synthesis the present methods of their preparation could be useful additions to the existing methodologies. Since α-nitroepoxides can be easily obtained from the corresponding nitroolefins via epoxidation with $NaOH/H_2O_2$ this procedure is extremely simple. General procedures for the preparation of 1,2-diones and α-iodoketones from α-nitroepoxides are described as follows : 1,2-Diones - A stirred mixture of α-nitroepoxide (1.6 mmol) in dry dimethyl sulfoxide (2 ml) and dichloromethane (0.2 ml) is treated with $ClSiMe_3$ (3.2 mmol) or $BF_3.Et_2O$ in dichloromethane (0.2 ml) at 0 °C. The resultant mixture is stirred for an additional time (see Table 1) at the same temperature. Triethylamine (5 mmol) dissolved in dichloromethane is then added dropwise to the above reaction mixture at 0 °C and stirring continued for an additional 1 h raising the temperature slowly to 30 °C. The reaction mixture is poured in cold water and extracted thoroughly with ethyl acetate. Evaporation of the solvent gives a crude product which is purified either by recrystallisation or chromatography. α-Iodoketones - A stirred mixture of sodium iodide (1.3 mmol) and α-nitroepoxide (1 mmol) in dry acetonitrile (2 ml) is treated with boron trifluoride etherate (1.3 mmol) in acetonitrile (1 ml) at 0 °C and the resultant mixture stirred at the same temperature until reaction is complete (see Table 1). The reaction mixture is then poured in cold water and extracted with ether. Evaporation of the solvent gives a crude product which is purified by preparative layer chromatography.

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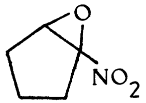
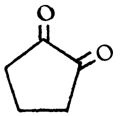
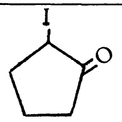
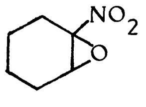
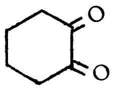
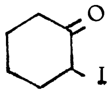
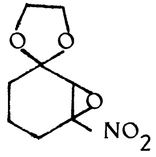
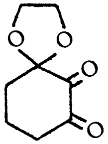
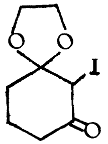
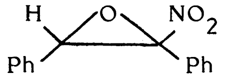
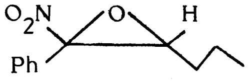
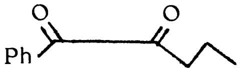
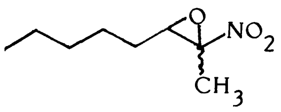
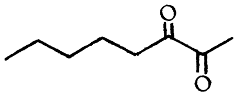
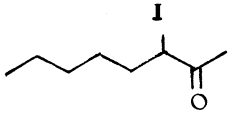
Table 1. Conversion of α-Nitroepoxides into 1,2-Diones and α-Iodoketones

Entry	α-Nitroepoxide	1,2-Dione	% Yield using $BF_3 \cdot Et_2O$	$\frac{\text{Time}}{\text{h}}$	% Yield using $ClSiMe_3$	$\frac{\text{Time}}{\text{h}}$	α-Iodoketone	% Yield	$\frac{\text{Time}}{\text{h}}$
1.			64	8	72	5		72	5
2.			64	10	75	6		75	6
3.			61	34	60	30	 7)	-	-
4.			77	7	87	4		81	9
5.			54	10	57	7		68	8
6.			60	11	65	7		71	8

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3) H. Newman and R.B. Angier, Tetrahedron, 26, 825 (1970).

4) M. Ashwell and R.F.W. Jackson, J. Chem. Soc., Chem. Comm., 1988, 282.

5) S. Kumazawa, T. Sakakibara, R. Sudoh and T. Nakagawa, Angew. Chem., 85, 992 (1973).

6) Y.D. Vankar and G. Kumaravel, Tetrahedron Lett., 25, 233 (1984) and references cited therein.

7) The product does form as indicated by the IR spectrum and the TLC of the crude reaction mixture (although the reaction is slow) but it decomposes during purification.

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